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On progressive polishing, the conductivity increased markedly and deviated markedly from the (approximate) T^3 behavior of the rough samples, as with silicon. A good fit to the measured κ vs. T curves was obtained by taking into account the scattering by the isotopes, the polished side surfaces, and the rough end surfaces. For the side surfaces, Ziman's theory [12] of diffraction by the surface irregularities in an infinitely long crystal was employed. Although the form of the resulting curves fit the data well, the required values of the roughness parameter seem anomalously small. However, the silicon data are equally well fitted by comparable values of this parameter.

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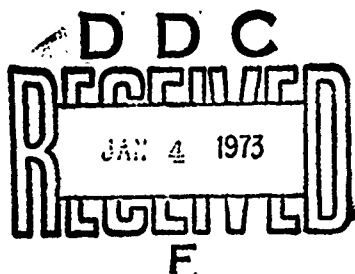
BOUNDARY SCATTERING OF PHONONS IN GERMANIUM AND SILICON

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ABSTRACT

Measurements of low-temperature thermal conductivity κ have been made on high-purity Ge single-crystal samples with various degrees of surface polish, to complement similar measurements previously reported [2] on silicon. As a result of the more pronounced isotopic impurity content, bulk scattering could not be completely eliminated even in our thinnest (~0.5 mm) and roughest samples. Accordingly, a Calloway-type [10] analysis was used in order to extract the boundary-limited mean free path.

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I. INTRODUCTION

At low temperatures in electrically insulating crystals, only two classes of phonon scattering processes are present: "normal" (momentum-conserving) three-phonon processes, and collisions with fixed imperfections. Among the latter are the surface of the crystal and, in the bulk, dislocations, point defects, chemical and isotopic impurities, etc. The analysis of heat transport in the presence of more than one scattering mechanism is exceedingly complicated. Fortunately, many materials are now obtainable in sufficient purity and perfection that the bulk defect scattering is negligible. The surface is then the primary barrier to the unimpeded flow of heat.

In recent years, there has been a marked increase in interest in this "boundary-scattering" regime, with regard to both the understanding of the fundamental scattering processes, and the use of the phenomena as a probe for the surface region of a crystal. Recent experimental measurements include those of Thacher [1] on LiF, Hurst and Frankl [2] on Si, McCurdy et al [3] on CaF and Si, and Bird and Pearlman [4] on Ge. Most of these measurements were made on rough-surfaced crystals. With the exception of Reference [2], the early work of Berman, Foster, and Ziman [5], and the present work, little attention has been paid to the extremely interesting case of highly specular surfaces.

The theory for the boundary-scattering regime is rather more complicated than ordinary bulk transport theory, since not only the kinematical properties of the carriers but also the points of origination of their "flight paths" must be taken into account. Thus, in the general case, one is faced with six-

dimensional integrals over both wave-vector space and real space. However, in the absence of bulk scattering, all flight paths originate at the surface, and the integrals reduce to five dimensions. These have been evaluated in certain cases:

1. Casimir [6] considered infinitely long circular and square cylinders of elastically isotropic material with perfectly rough (diffuse) surfaces. His classic result may be put in the form

$$\kappa_{iso} = \frac{1}{3} C <S> \ell_c, \tag{1}$$

where C is the specific heat, $<S>$ is an appropriate average sound speed (averaged over the three acoustic modes) and ℓ_c is the so-called "Casimir length", given by

$$\ell_c = \begin{cases} 2R \text{ for a circular cylinder,} \\ 1.12 \ W \text{ for a square cylinder,} \end{cases} \tag{2}$$

where R and W are, respectively, the radius of the circle or the side of the square.

2. Berman, Simon, and Ziman [7] extended the calculations to include finite length L and non-zero "specularity factor" P for circular cylinders. The result was that ℓ_c was replaced by a corrected length ℓ:

$$\ell = \ell_c \ F(R/L, \ P). \tag{3}$$

For an infinitely long circular cylinder, the correction factor is

$$F(0, \ P) = (1 + P)/(1 - P). \tag{4}$$

3. The experimental results of Hurst and Frankl [2] and of McCurdy et al [3] as well as certain heat-pulse effects [8], made it clear that the elastic anisotropy played a highly significant role. The key factor, as pointed out by McCurdy et al, is that the phonons travel with the group velocity rather than the wave velocity (ordinary sound velocity). On this basis, they were able to calculate the conductivity of finite-length, rough-surfaced, circular, square, and rectangular cylinders in good agreement with experiment. Needless to say, their results reduced to Eq. (1) in the appropriate limits.

II. EXPERIMENTAL

A. Method

Oriented germanium rods were cut from a single crystal of high chemical purity and of the natural isotopic mixture, with an abrasive-wire saw. Rough surfaces were prepared by lapping with 600-grit SiC (particle size ~9μ) on a glass block, followed by sand-blasting. Diamond polishing was done with 6μ and 1μ powder paste starting on a power-driven cloth lap and finishing by hand on a lens-paper lap. Further polishing was done with a commercial preparation called Lustrox.[1] Samples were square cylinders, typically about 1 mm wide x 40 mm long, and usually oriented in the [100] direction with faces of {110}-type. Thermal conductivity measurements were made by the standard two-heater method in a He^4 cryostat, using germanium resistance thermometers. Details are given in Reference [2].

[1] Sold by Tizon Chemical Corp., Flemington, New Jersey, U.S.A.

B. Results for Silicon

The results previously reported [2] may be summarized as follows:

1. For rough-surfaced crystals, the expected T^3-dependence was reasonably well born out; actual values of $d(\log \kappa)/d(\log T)$ lay mainly between 2.90 and 3.00. The size dependence followed roughly the form of Eq. (2).

2. There was a pronounced anisotropy in the conductivity, the [100] direction being roughly twice as large as the [110] or [111].

3. On polishing, the conductivity increased markedly, especially at the lower temperatures. Apparent P values > 0.9 were obtained in a few cases.

C. Results for Germanium

Figure 1 shows typical data for rough-surfaced (sand-blasted) rods. It will be noted that $d(\log \kappa)/d(\log T)$ falls considerably below 3.0 even at the lowest temperatures. This, it will be seen later is a result of the isotope scattering. The size effect data tend to substantiate Eq. (3) within about ±5%, the shape correction factors being close to 1.0 for these samples. The values agree well (at 2°) with the pure [100] sample (sample 2) of Carruthers et al [9]. In contrast, the data reported by Bird and Pearlman [4] for their "pure" sample lie about 20% lower, after correcting for the size difference and the shape factor $F \approx 0.85$. Possibly the discrepancy is due to the rather short rods used by these authors.

Figure 1 also illustrates the anisotropy, which is seen to be somewhat less pronounced than in silicon. In passing, it may be mentioned that we have also observed anisotropy in the same sense in LiF, although the reproducibility of the data was not very good.

	l_c (mm)
+ [100]	2.24
o [100]	1.63
× [111]	1.64

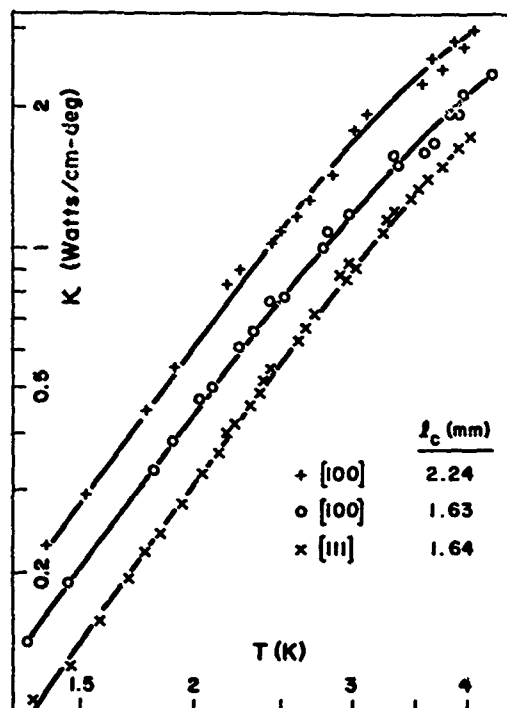|	l_c (mm)
× LUSTROX	1.31
o 1μ DIAMOND	1.48
+ SANDBLAST	1.41

Figure 1. Thermal conductivity of rough-surfaced germanium rods.
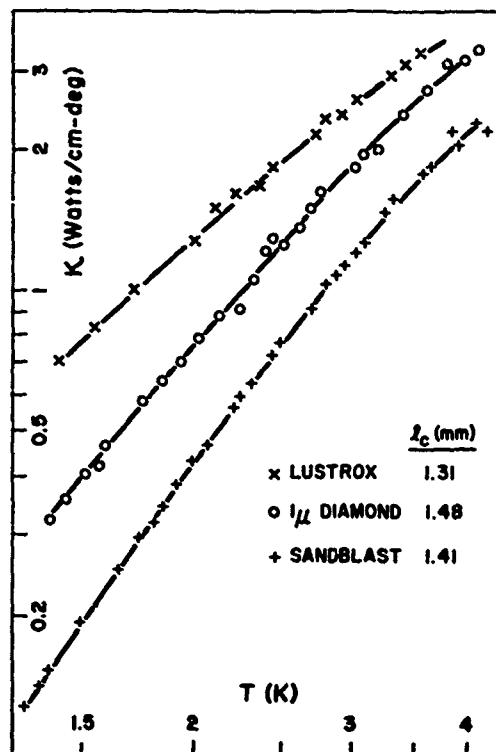
Figure 2. Effect of polishing on thermal conductivity of germanium [100] rods.

The effects of progressive polishing are illustrated in Figure 2. Qualitatively they are the same as in silicon, although the more serious isotope scattering lowers the conductivity very considerably. It will be noted that the enhancement factor is again considerably greater at the lower temperatures, showing that the specularity factor P must be dependent on the phonon wavelength.

Several attempts ' ~ve been made to improve the surface smoothness still further by chemical etching between the various mechanical abrasion processes. The intent here was to reduce to a minimum the amount of damaged material in the sample. The main result has been to make it extremely difficult to obtain reliable data, owing to very poor thermal contact of the thermometers to the samples. The same difficulty was encountered with silicon, but not as severely. One remedy attempted was to sandblast a small strip under each thermometer clamp. However, the small region of diffuse surface produced an appreciable decrease in conductivity, so this approach was abandoned. Work along these lines is still in progress.

III. ANALYSIS OF THE DATA

A. Wavelength Dependence of Specularity Factor

We first consider an approximate analysis in which the anisotropy effects are ignored. The main features dealt with are (a) the increasing departure from T^3-dependence as the surface smoothness increases, and (b) the separation of surface and bulk scattering. The standard method for analysis of mixed scattering is via the theory of Callaway [10] as amended by Holland [11]. Accordingly, we write

$$\kappa = \sum_{i=1}^{3} \frac{k_B^4 T^3 / \hbar^3}{6\pi^2 S_i} \int_0^\infty \frac{x^4 e^x \, dx}{(e^x - 1)^2 \tau_i^{-1}}. \tag{5}$$

where $i = 1$ designates the longitudinal modes, $i = 2, 3$ the transverse modes, S_i is an appropriate direction-averaged sound velocity for the ith mode-type, and the other symbols have their usual meanings. The inverse relaxation times were written as

$$(\tau_i)^{-1} = (\tau_{isotope})^{-1} + (\tau_N)^{-1} + (\tau_{B,i})^{-1}. \tag{6}$$

The isotope scattering and normal-process scattering terms were taken from Holland [11] as

$$(\tau_{isotope})^{-1} = A\omega^4 = A(k_B T/\hbar)^4 x^4, \tag{6}$$

and

$$(\tau_N)^{-1} = B\omega^2 T^3 = B(k_B/\hbar)^2 T^5 x^2, \tag{7}$$

with $A = 1.32 \times 10^{-44}$ sec^3, $B = 3.8 \times 10^{-24}$ sec deg^{-3} for silicon, $A = 2.57 \times 10^{-44}$ sec^3, $B = 2.77 \times 10^{-23}$ sec deg^{-3} for germanium. The values of $(\tau_N)^{-1}$ were negligible throughout, and thus the exact form chosen in Eq. (7) is inconsequential.

For the boundary scattering, we wish to take into account the specularity of the surfaces and the finite length of the rods. As noted previously, the progressive departure from T^3-dependence makes it clear that the specularity is wavelength-dependent. On general grounds, it could be expected to be angle-dependent also, but there is no way of incorporating this into a theory of the present type. Ziman [12] and Soffer [13] have considered the problem of reflection of waves from rough surfaces. Soffer obtains, in the limit of no lateral correlation in the surface roughness

$$P(k) = \exp [-(2k\eta_{eff})^2], \tag{8}$$

where $\eta_{eff} = \eta \cos \theta_{inc}$, $\qquad\qquad\qquad\qquad\qquad$ (8a)

k = magnitude of phonon wave-vector, θ_{inc} = angle of incidence, and
η = rms height deviation in the surface. Then, in view of Eq. (3), we
take as a plausible averaged expression

$$(\tau_{B,i})^{-1} = S_i \left[(\ell_c)^{-1}(1 - P)/(1 + P) + (L)^{-1} \right]. \qquad (9)$$

The foregoing expressions were gathered into Eq. (5) and the integrals
computed for various values of η_{eff}. Results are shown in Figures 3 and 4.
In these calculations, the velocities used for the transverse modes were
averages of the type calculated by Hasegawa [14], viz., 5.42×10^5 cm/sec for
Si and 3.29×10^5 cm/sec for Ge. There is, of course, no reason to assume
this to be a correct average in the present context, but it is seen that the
resulting fit for the rough-surfaced samples of both materials is reasonably
good, with no adjustable parameters. Clearly, some slight adjustments of the
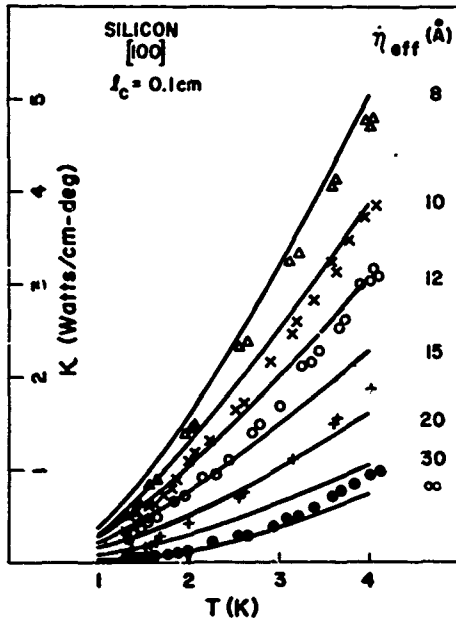velocities could improve the fits.

Figure 3. Fit of Eqs. (5) - (9) to
data on silicon. Lowest set
of points for rough surface,
next for 1μ diamond polish,
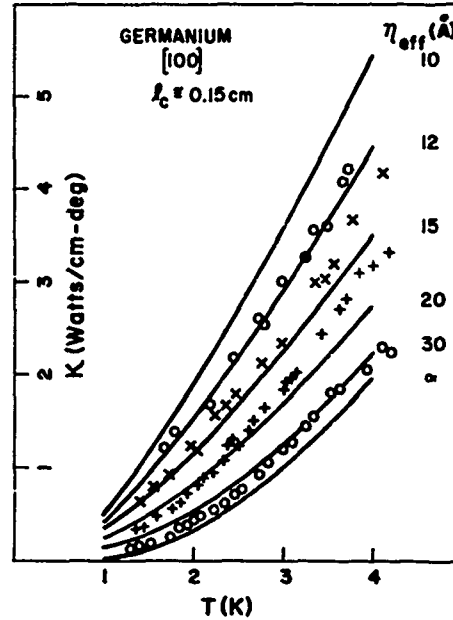upper three for Lustrox
polish.

Figure 4. Fit of Eqs. (5) - (9) to
data on germanium. Lowest
set of points for rough
surface, next for 1μ
diamond polish, upper two
for Lustrox polish.

The curves for partly specular surface (finite values of η_{eff}) form a
family that seems to represent the observed temperature dependences
reasonably well. Furthermore, the apparent values of η_{eff} are comparable for
the two materials at each stage of polishing. These values are, to be sure,
surprisingly small in relation to the grit sizes used in the polishing. They
can possibly be understood, however, as a result of the $\cos \theta_{inc}$ factor in
Eq. (8a), which would lead to an overwhelming preference for those phonons
traveling nearly parallel to the rod axis.

B. Directional Dependence of Specularity Factor

In order to help decide whether the basic mechanism (i.e., diffraction)
discussed in the preceding section may be the correct one, it would be

desirable to extend the anisotropic transport theory of McCurdy et al [3] to the case of partly specular reflection. However, the problem is a very complicated one. Among the effects to be considered are the following:

1. The factor $(1 + P)/(1 - P)$ is valid only for an isotropic circular rod, in which successive reflections yield identical flight paths. In a square rod, there are different reflected flight paths depending on the original point of emission, and there are two distinct angles of incidence, hence two P-values.

2. The result of a specular reflection is to preserve momentum components, not velocity compoenents. A consequence, according to Price [15], is that specular reflection does produce resistance. Thus, the $(1 + P)/(1 - P)$ factor is wrong even in the limit $P \to 1$.

3. When a single mode is reflected, the general result is that at least two reflected waves are required in order to satisfy the boundary condition [16]. Thus, instead of a single function $P(k)$, we need a matrix $P_{ij}(k)$ connecting the various modes.

Conceivably, this last point could hold the key to the explanation of our anomalous values of n_{eff}. In effect, we find that the polishing increases the conductivity by an unexpectedly large factor. This could occur if there were a net transfer of phonons to more "efficient" modes. In fact, according to Thurston [16], this is just what occurs: a transverse wave (slow), produces a reflected longitudinal wave (fast), which moves more nearly parallel to the surface. Beyond a critical angle, the latter becomes a Rayleigh wave, which might in a good sample be virtually un-attenuated.

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